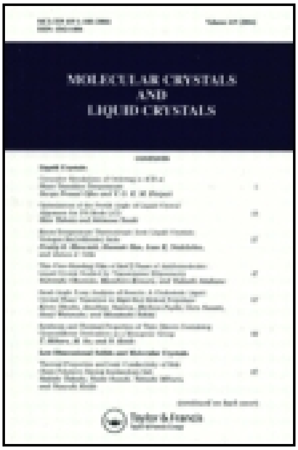

Molecular Crystals and Liquid Crystals

Investigation of the Visco-Elastic Properties of Mixtures with Different Birefringence

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INVESTIGATION OF THE VISCO-ELASTIC PROPERTIES OF MIXTURES WITH DIFFERENT BIREFRINGENCE

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The STN switching mechanism is governed by elastic constant ratios K_{33}/K_{11} and K_{22}/K_{11} (K_{11},K_{22} and K_{33} are respectively the splay, twist and bend elastic constants). This work explores the limitation of K_{22}/K_{11} and how this can be translated into material/mixture design.

The visco-elastic parameters K_{11}, K_{22}, η_{splay} and γ_1, were measured by dynamic light scattering (DLS) for three mixtures, based respectively on cyanobiphenyls, phenylbenzoates and dicyclohexyls with birefringence Δn ranging from 0.05 to 0.2. This study confirms that K_{22} and K_{11} only show slight variation for these mixtures; therefore, the ratio of K_{22}/K_{11} remains remarkably constant and cannot be exploited in material design.

In contrast, the twist and splay viscosities are directly related to the composition of the mixtures. Strongly polar nematic liquid crystals, such as the cyanobiphenyls, exhibit higher rotational viscosity coefficients.

This work also outlines the dependence of the measurement accuracy of the visco-elastic parameters on the birefringence of the material investigated.

Keywords: birefringence; dynamic light scattering; elastic constants; rotational viscosity

4.1 DYNAMIC LIGHT SCATTERING: THEORY

Orsay theory predicted that in nematic crystals, the Lorentzian frequency broadening is due to quasi-elastic scattering from two overdamped director

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fluctuation modes [1]. Mode 1 corresponds to splay-bend distortions whilst mode 2 consists of twist bend deformations. Using particular scattering geometries and specific input and output polarizations, it is possible to isolate each mode. For pure splay and twist modes in the presence of a damping electric field, the linewidths are given by [1–5]:

For pure splay mode:

$$\Gamma_1 = \frac{K_{11}\, q_\perp^2}{\eta_{\rm splay}} + \frac{\varepsilon_0\, \Delta\varepsilon\varepsilon_\parallel\, V^2}{\eta_{\rm splay}\left(\varepsilon_\perp + \Delta\varepsilon \sin^2\left(\frac{\theta_{\rm lab}}{2}\right)\right) d^2}. \tag{1}$$

For pure twist mode:

$$\Gamma_2 = \frac{K_{22}\, q_\perp^2}{\gamma_1} + \frac{\varepsilon_0\, \Delta\varepsilon\, V^2}{\gamma_1\, d^2}. \tag{2}$$

where $q_\perp = (2\pi/\lambda)\sin\theta_{\rm lab}$ is the component of scattering wavevector perpendicular to the director ($\theta_{\rm lab}$ is the scattering angle in the laboratory frame), V is the applied rms voltage and d is the sample thickness; ε_0 is the vaccum permittivity, $\varepsilon_\parallel$, $\varepsilon_\perp$ are the dielectric constants and $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 0$ is the dielectric anisotropy of the nematic. K_{11} and K_{22} are the Frank elastic constants associated respectively with splay and twist deformations. $\eta_{\rm splay}$ and γ_1 are the associated viscosity coefficients defined in terms of the Leslie coefficients α_i as [1]:

$$\eta_{\rm splay} = \gamma_1 - \frac{2\alpha_3^2}{\alpha_3 + \alpha_4 + \alpha_6} \tag{3}$$

$$\text{and} \quad \gamma_1 = \alpha_3 - \alpha_2. \tag{4}$$

For most nematics, α_3 is much smaller than the other Leslie coefficients and therefore, to a good approximation $\gamma_1 \approx \eta_{\rm splay}$. From the resultant quenching of the director fluctuations, the elastic constants and viscosity coefficients can be separated. Thus it is possible to determine each parameter individually, provided the dielectric constants of the material are known.

4.2 EXPERIMENTAL

4.2.1 Materials

The three mixtures were provided by Merck NB-SC(UK) and each contains several low molar mass mesogenic components based on cyanobiphenyls (A), phenylbenzoates (B) and dicyclohexyls (C). These mixtures are characterized by different optical anisotropies. Table 1 below summarizes the main properties of each sample.

TABLE 1 A, B and C Mixtures with their Main Constituents and their Clearing Points

Mixture	Clearing point T_{NI}	Birefringence
Cyanobiphenyls (A)	35 °C	high
Phenylbenzoates (B)	35 °C	medium
Dicyclohexyls (C)	45 °C	low

4.2.2 Dynamic Light Scattering (DLS)

The experimental set-up is shown in Figure 1. Photon correlation experiments were performed in the heterodyne detection mode using a 10 mW red He-Ne laser ($\lambda = 632.8$ nm) as the incident light source. Two dichoric polarisers define the incident and scattered light polarisations. The

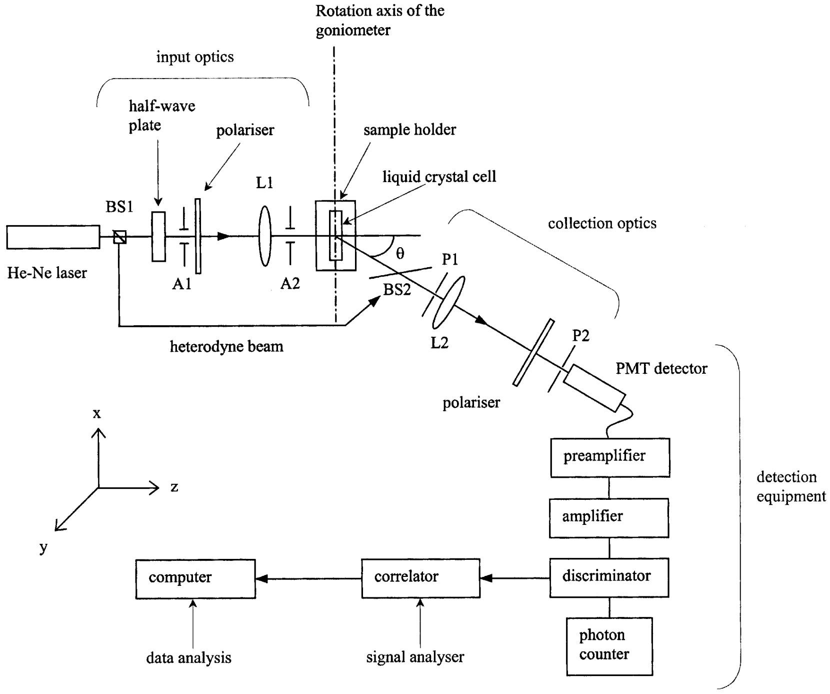

FIGURE 1 Schematic diagram of the light scattering spectrometer and detection equipment (BS1 and BS2 are beam splitters, A1 and A2 are two variable apertures, L1 and L2 are two convergent lenses, P1 and P2 are 200 µm diameter pinholes).

collection optics can be rotated in the horizontal plane and the scattering angles are measured using a Vernier scale. A scattering angle $\theta_{\text{lab}} = 14^{\circ}$ was chosen in order to minimise the bend component to the twist and splay fluctuation modes. In this scattering geometry, the twist mode is isolated for a horizontal output and vertical light input polarisations while the splay mode is isolated if both incident and scattered light polarisations are within the scattering plane. The detection equipment consists of a photomultiplier (PMT) tube, an amplifier and a discriminator to improve the signal-to-noise ratio. Finally, the resulting signal is fed into a photon counter and a 128 channel digital auto-correlator. The data from the correlator are collected and analysed by a PC computer. The linewidth corresponding to each mode can be obtained by fitting the autocorrelation function of the scattered light intensity using a least-square Marquadt algorithm.

The voltage signal from a function generator is amplified to 30 V for application across our cells. It was found that for a 10 kHz square wave signal there was no dependence of the linewidth on the frequency [5].

The cells used for DLS experiments, of thickness between 44 and 46 μm, were made of ITO glass coated with a 1% solution of lecithin in chloroform to induce homeotropic orientation.

4.2.3 Other Techniques

The static dielectric permittivities were determined to within ±1% accuracy by a capacitance techique using homeotropic aligned cells to obtain $\varepsilon_{\|}$ and planar cells to measure $\varepsilon_{\perp}$. The measurements were carried out on a Wayne-Kerr 6425 multi-bridge with a probe voltage of 200 mV at a frequency of 10 kHz, which is the same frequency as the applied electric field in DLS experiment.

The measurements of refractive indices were performed using a Bellingham and Stanley HR60 Abbé refractometer with a He-Ne laser light source. The sample is aligned homeotropically between the two prisms. The extraordinary refractive index n_e is obtained with the light polarised vertically (parallel to the molecular long axis) and the ordinary refractive index n_o with the light polarised horizontally. The uncertainty on the birefringence $\Delta n = n_e - n_o$ is ±0.002.

4.3 RESULTS AND DISCUSSSION

4.3.1 Dielectric and Optical Properties of the Mixtures

The values for the dielectric anisotropy $\Delta\varepsilon$ and birefringence Δn measured for each mixture are plotted versus relative temperature T_{NI}-T in Figures 2 and 3 respectively. The dielectric anisotropy is significantly higher for the

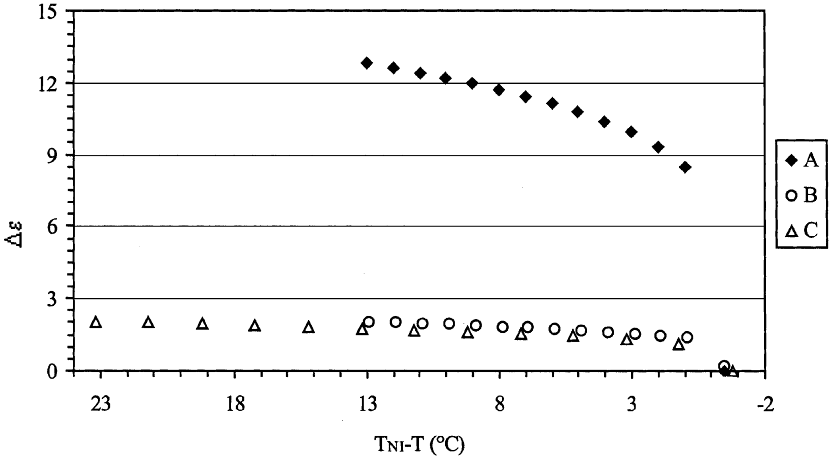

FIGURE 2 Dielectric anisotropy of the A, B and C mixtures.

mixture of cyanobiphenyls ($8.5 \leq \Delta\varepsilon \leq 13$) than for the samples containing phenylbensoates or dicyclohexyls. This increase is due to the presence of LC molecules with strongly polar nitrile groups in sample A. The dielectric properties of B and C are quite similar; their $\Delta\varepsilon$ values are low (between 1 and 2), almost constant and show a weaker temperature dependence than in the case of sample A. The three mixtures have very different optical behaviour: the sample with cyanobiphenyls is a high birefringence mixture ($0.15 \leq \Delta n \leq 0.2$), the mixture of dicyclohexyls is a low birefringence

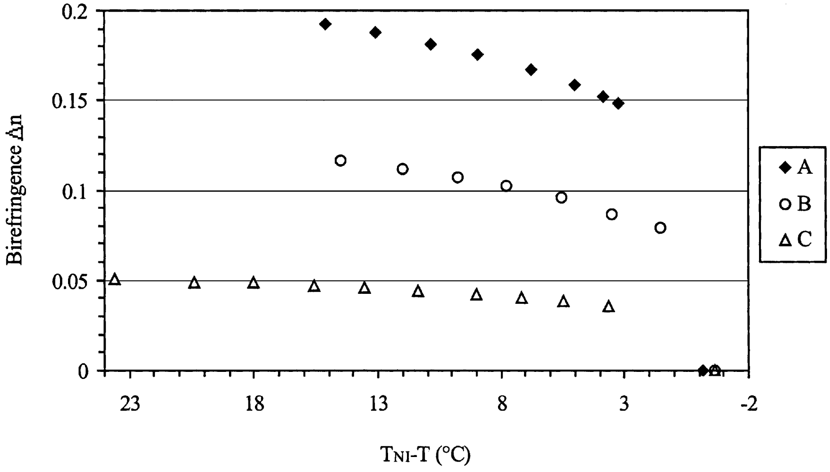

FIGURE 3 Optical anisotropy of the mixtures A, B and C.

mixture ($0.03 \leq \Delta n \leq 0.05$) while the sample containing phenylbenzoates exhibits intermediate values of Δn ($0.08 \leq \Delta n \leq 0.12$).

4.3.2 Visco-elestic Properties

The twist and splay elastic constants K_{11} and K_{22} and associated viscosity coefficients were determined at the same shifted temperature, in order to compare the three mixtures. Table 2 summarises all visco-elastic results, as well as the dielectric anisotropy and birefringence data taken at T_{NI}-$T = 13$°C.

Neither K_{22} nor K_{11} change significantly with mixture composition. Therefore, the three samples have similar twist-to-splay elastic constant ratio if the experimental errors on K_{22} and K_{11} are taken into account. This ratio does not vary with mixture compostion or nature [6], which is confirmed in this work. K_{22}/K_{11} has been found experimentally to range from 0.5 to 0.7 for most nematic materials [6] (if pre-transitional effects are excluded).

For samples with cyanobiphenyls and phenylbenzoates, the rotational viscostiy γ_1 can be determined with an accuracy of $\pm 2\%$ with values of the same order of magnitude i.e. between 80 and 95 mPa.s. Furthermore, the splay viscosity η_{splay} is equal to γ_1 within experimental uncertainties for these two samples. By contrast, in the case of the dicyclohexyl compounds, γ_1 is reduced by approximately a factor of 5 (its value is about 18 mPa.s). In general, higher rotational viscosity coefficients are associated with strongly polar materials, [6] such as the cyanobiphenyls. For the dicyclohexyl mixture, η_{splay} is much lower than γ_1, which would lead to a negative value for $\frac{2\alpha_3^2}{\alpha_3+\alpha_4+\alpha_6}$. This result can be interpreted as a greater experimental error on the viscosities of about $\pm 6\%$ for the dicyclohexyls due to the weaker scattered signal from this low birefringence sample, as

TABLE 2 Summary of the Physical Properties of the Tree Mixtures at T_{NI}-$T = 13$ °C

	Cyanobiphenyls	Phenylbenzoates	Dicyclohexyls
T(°C)	22	22	32
T_{NI}-T(°C)	13	12.9	13.2
$\Delta n \pm 0.002$	0.188	0.114	0.046
$\Delta\varepsilon \pm 1\%$	12.8	2.1	1.8
k_{22}(pN)	3.7 ± 0.1	3.5 ± 0.1	3.3 ± 0.2
k_{11}(pN)	5.9 ± 0.3	6.4 ± 0.3	5.9 ± 0.4
k_{22}/k_{11}	0.63 ± 0.03	0.55 ± 0.03	0.56 ± 0.04
γ_1(mPa.s)	84 ± 2	92 ± 2	18 ± 1

TABLE 3 Experimental Data for the Three Mixtures at T_{NI}-T = 13°C for the Twist Mode

	Mixture A	Mixture B	Mixture C
Scattered signal (for one run)	75 kHz	58 kHz	20 kHz
Experimental duration	40 s × 25 runs	40 s × 30 runs	100 s × 30 runs
Twist linewidth	254.7 Hz	221 Hz	1161.8 Hz
Noise factor	0.01%	0.013%	0.055%

illustrated in Table 3. Though the experimental duration is increased to 3000 s for this mixture, the number of scattered photons is still significantly reduced compared to the samples containing cyanobiphenyls and phenylbenzoates. From the data collected in Table 3, there is a direct correlation between the birefringence of a material, its scattering behaviour and the noise factor associated with the measured linewidth. The noise factor, is a measure of the accuracy of the fitted data with respect to the experimental values.

4.4 CONCLUSION

This work shows that the chemical structures of the mixtures and their polarities have a small effect on the twist and splay elastic constant [7]. Both K_{11} and K_{22} depend to a certain extent on the geometrical factors characteristic of a given mesogenic molecule, although the influence of the molecular shape is extremely complex to quantify in the case of mixtures of several components. The ratio K_{22}/K_{11} is remarkably constant for mixtures of different chemical nature. In contrast, the twist and splay viscosities are directly related to the polarity and the composition of the mixtures. Strongly polar nematic liquid crystals exhibit higher rotational viscosity coefficients [6]. This study also confirmed that the accuracy of the measurements of visco-elastic parameters depends on the birefringence of the material investigated.

DLS still gives reliable order-of-magnitude information on the viscosity but in the case of mixture C, the absolute viscosity is obtained with an accuracy of ±6% while for samples A and B, the uncertainty is only ±2%. This also leads to further errors on the elastic constant values for sample C.

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